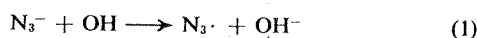


Absorption Spectra and Kinetics of the Intermediate Produced from the Decay of Azide Radicals

Sir:

Azide ions in aqueous solution undergo a one-electron oxidation mechanism on reaction with hydroxyl radicals



This reaction has been studied by generating OH radicals in the pulse radiolysis of aqueous solutions, in the presence of 1 atm of nitrous oxide to convert >98% of e_{aq}^- to OH radicals. Single pulses of 2.3-MeV electrons and 30-nsec duration were used; all experimental details have been described.¹ Figure 1

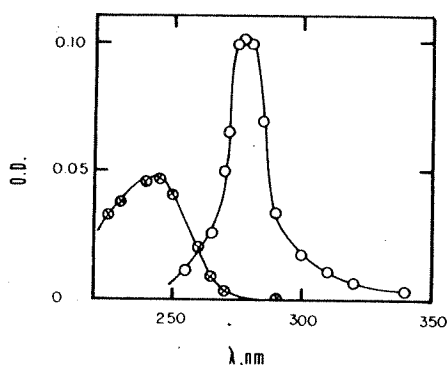
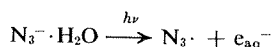


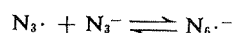
Figure 1. Transient absorption spectra produced from the reaction of OH radicals with 1 mM N_3^- ions in aqueous solution at pH 9.2. OD measured at 0.1 μsec (O) and 10 μsec (X) after a 30-nsec single pulse of electrons, total dose 4 krad. Identical spectra observed in the presence of 0.1 M NaCl and in 10 M NaN_3 .

shows the transient absorption spectrum obtained immediately after the pulse—this band has a λ_{max} at 278 nm, and is assigned to the $\text{N}_3\cdot$ radical. An identical spectrum has recently been obtained,² and similarly identified, in the flash photolysis of N_3^- ions in its CTTS band



Based on $G(\text{OH}) = 5.6$, the extinction coefficient of $\text{N}_3\cdot$ is found to be $\epsilon_{278} 2.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The azide radical decays by a second-order process with $2k = 9 \pm 1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, in excellent agreement with the value $9.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ obtained from flash photolysis work.² The rate constant $k(\text{OH} + \text{N}_3^-) = 1.2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ was obtained, based on kinetic competition with the benzoate ion, and taking³ $k(\text{OH} + \text{PhCOO}^-) = 6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.

Azides resemble halides and in many respects react like pseudohalides. They do not, however, appear to produce N_6^- radicals



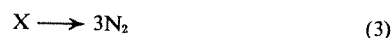
similar to $\text{Cl}_2\cdot^-$, $\text{Br}_2\cdot^-$, and $\text{I}_2\cdot^-$ radicals. The absorption maximum, the decay rate, and the extinction coefficient of the 278-nm band were found to be independent of $[\text{N}_3^-]$ in the range 0.4–10 mM. The decay kinetics at 280 nm were found to be independent of the ionic strength of the solution (up to 0.2 M Na_2SO_4), indicating the absence of a charge on the radical. Finally, in the presence of 0.1 M Cl^- ions the $\text{N}_3\cdot$ band was unchanged, suggesting the absence of the complex $\text{N}_3\cdot + \text{Cl}^- \rightleftharpoons \text{N}_3\text{Cl}\cdot^-$.

Concomitant with the second-order decay of the $\text{N}_3\cdot$ radical is the formation of another intermediate with λ_{max} at 242 nm; see Figure 1. This new species X is produced by a second-order process with $2k = 6.2 \times 10^6 \epsilon_{242} \text{ M}^{-1} \text{ sec}^{-1}$

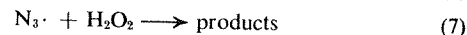
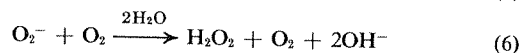
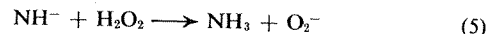


Assuming this mechanism, ϵ_{242} is $2.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, and the rate of formation of X is $2k = 1.3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, in good agreement with the rate of decay of $\text{N}_3\cdot$ radicals at 278 nm.

The intermediate X decays by a first-order process to give nitrogen



with $k_3 = 3.6 \times 10^3 \text{ sec}^{-1}$, i.e., $\tau_{1/2}$ of $\sim 200 \mu\text{sec}$. In support of reactions 2 and 3, the yield of N_2 in this system was determined, since in earlier work⁴ complicated factors involving the reaction of e_{aq}^- were not eliminated. ^{60}Co γ irradiation of 10^{-2} M NaN_3 , pH 8.5, saturated with N_2O gave a $G(\text{N}_2) = 11.0 \pm 0.4$, $G(\text{H}_2) = 0.33$, and $G(\text{O}_2) = 0.37$. Assuming $G(\text{OH}) = G(e_{\text{aq}}^-) = 2.8$, $G(\text{H}) = 0.6$, $G(\text{H}_2) = 0.45$, and $G(\text{H}_2\text{O}_2) = 0.72$, a $G(\text{N}_2) = 11.8 \pm 0.4$ can be expected, based on reactions 1–3. The formation of O_2 and the slightly lower yield of N_2 observed could be due to



where $k_4 = 7.3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ (ref 5). Under the above experimental conditions, the reaction of $\text{N}_3\cdot$ with H_2O_2 plays only a minor part.

It is interesting to speculate on the nature and structure of the intermediate X. The azide ion⁶ is linear and symmetrical, and since removal of an electron from the nonbonding orbital is expected to have almost no effect on the bond lengths, vibration frequencies, and force constants, $\text{N}_3\cdot$ can be said to resemble closely N_3^- . Dimerization of N_3 is not forbidden by spin-conservation rules and, thermochemically, is highly

(3) P. Neta and L. M. Dorfman, *Advan. Chem. Ser.*, No. 81, 222 (1968). The CNS^- method could not be used since $(\text{CNS})_2^-$ undergoes a fast reaction with N_3^- ions.

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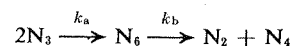
(6) See review by P. Gray, *Quart. Rev., Chem. Soc.*, 17, 441 (1963).

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(2) A. Treinin and E. Hayon, *ibid.*, 50, 538 (1969).

favorable,⁶ with $\Delta H = -210 \pm 6$ kcal/mol for the overall reaction $2\text{N}_3 \rightarrow 3\text{N}_2$. Indeed this could account, in part, for the explosion and detonation decomposition of azide crystals. It is tentatively suggested that the nature of the intermediate X is N_6 . The structure of N_6 could be either extended or cyclic. The following points could be used in support of a cyclic structure, similar to that of the benzene ring: (a) the nitrogen atom is isoelectronic with the $-\text{CH}-$ radical, and this endows it with similar physical properties of molecular symmetry and structure; (b) the absorption maximum of N_6 is close to the first absorption band of benzene⁷ ($\lambda_{\text{max}} \sim 255$ nm and $\epsilon \sim 200 \text{ M}^{-1} \text{ cm}^{-1}$); (c) the electrolysis of aqueous solutions of $^{14}\text{N}^{15}\text{N}^{14}\text{N}$ gave⁸ no $^{15}\text{N}_2$ but $^{14}\text{N}_2 + 2^{14}\text{N}^{15}\text{N}$. An extended structure for N_6 could be related to 1,3,5-hexatriene, which has absorption maxima⁹ at 251, 244, 241, and 234 nm and $\epsilon \sim 6000 \text{ M}^{-1} \text{ cm}^{-1}$. It is interesting to note that the gas-phase photolysis⁹ of 1,3,5-hexatriene produces benzene and other cyclic products. The exothermicity of reaction 3 could induce the cyclization of the intermediate N_6 .

Alternatively, the decay of $\text{N}_3\cdot$ could give rise to



If the intermediate X is N_4 , the kinetics require that $k_b \gg k_a$. Further work is in progress to elucidate the nature and structure of the 242-nm absorption band.

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(9) Reference 7, p 512.

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